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Research Article

Geospatial Statistics Elucidate Competing Geological Controls on Natural CO₂ Seeps in Italy

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Site selection for the geological storage of CO₂ for long timespans requires an understanding of the controls on containment, migration, and surface seepage of subsurface CO₂ fluids. Evidence of natural CO₂ migration from depth to the surface is documented at 270 sites from Italy, a prolific CO₂ province. Previous studies indicate that CO₂ delivery to and from buried structures that host CO₂ accumulations is fault controlled but competing controls on the CO₂ flow pathways affect the location and style of CO₂ release. Here, we conduct a meta-analysis using a novel geospatial approach to statistically determine the relationship between the geological setting and structures and the CO₂ seep spatial distribution and characteristics (morphological type, flux, and temperature) in Central Italy. We find that seep distribution differs on two spatial scales corresponding to the geological setting. On large scales (>5 km), seeps are isotropically distributed and align with regional structures such as anticlines, decollements, and extensional faults. On local scales (<5 km), seeps cluster and align with subsidiary geologic structures, including faults and lithological boundaries. The detailed location and flux of seeps within clusters are influenced by the regional structural domain: in the Tyrrhenian, seeps tend to be located along fault traces, whereas seeps are located as springs in the tip and ramp regions of fault scarps in the Apennines. Thus, our geospatial approach evidences, at a regional scale, how macrocrustal fluid flow is governed by deep extensional and compressional features but once CO₂ reaches shallower structures, it evidences how smaller scale features and hydrogeological factors distribute the CO₂ fluids in the near surface, dependent on the geological setting. This work not only demonstrates useful application of a novel geospatial approach to characterize competing crustal controls on CO₂ flow at different scales but also informs the design of appropriate site characterization and surface monitoring programs at engineered carbon stores.

1. Introduction

Carbon capture and geological storage (CCS) can significantly reduce anthropogenic CO₂ emissions from large industrial sources of CO₂ [1, 2]. However, for CCS to contribute effectively to climate change mitigation, the CO₂ must remain in the subsurface for tens of thousands of years [1, 3]. Examining naturally occurring CO₂ seeps allows quantitative examination of the diverse crustal pathways taken by CO₂ migrating from depth [4–7] and thus guides the selection of secure storage sites and the robust design of low-cost monitoring programs capable of detecting potential leakage to the surface. Further,

understanding of CO₂ flow pathways informs not only leak prevention but also leak remediation [8].

Natural CO₂ seepage is widespread in Italy [9], where 308 CO₂ seeps at 270 locations exhibit a variety of surface expressions (types), temperatures, and fluxes [10]. These seeps have already proven being valuable for studying the environmental and social impact of CO₂ escape [11, 12], storage site monitoring techniques [13], and CO₂ leak pathways [14, 15].

The location of subaerial CO₂ seeps in Italy is shown in Figure 1, along with major structural features. These structures are mostly derived from tectonic processes associated with the subduction of the Adria plate beneath the European margin [16, 17]. Initiating in the Miocene, NE-

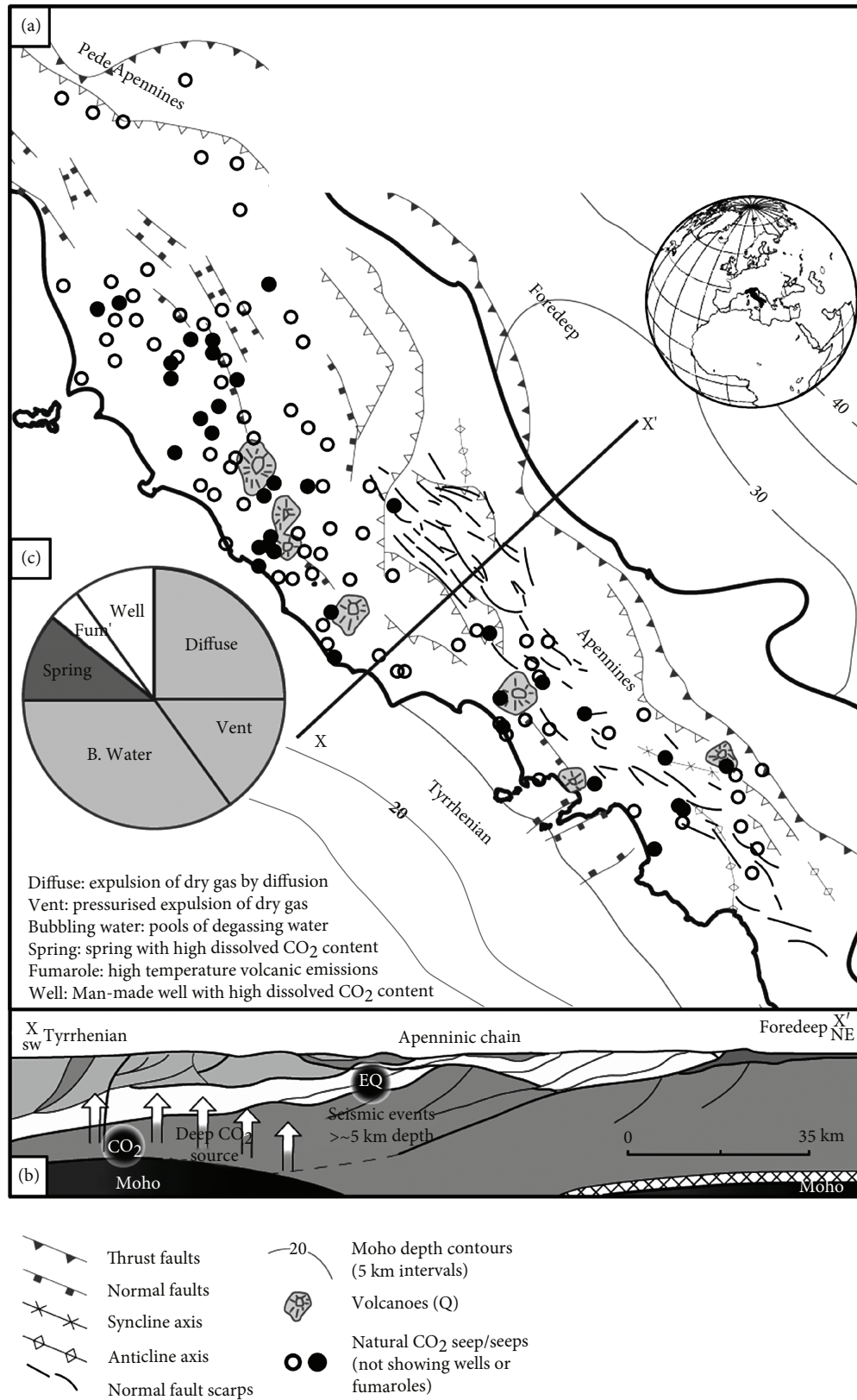


FIGURE 1: Schematic map of Italy showing the location of regional geological structures and Quaternary (Q) volcanoes (adapted from [25, 26]), CO₂ seeps [10] (where filled symbols indicate multiple seeps), Moho depth contours [27], and mapped normal fault scarps after [28]. Filled symbols show multiple seeps. Location of Italy shown on the globe inset. (b) Crustal cross-section of the Central Apennines modified from [17, 29, 30]. While earthquakes (EQ) and CO₂ delivery occur across the section, circles indicate the main, simplified occurrences. (c) Proportion of CO₂ seep types classified qualitatively according to surface expression.

SW compression caused tectonic stacking of Mesozoic-Tertiary carbonate platform and foredeep sediments which concentrated in a NE-migrating thrust belt. Coeval back arc extension thinned the crust in the Tyrrhenian sector, leading to high heat flow and active volcanism since the Pliocene and developing distinct NW-SE-trending structural domains shown in Figure 1—the thinned Tyrrhenian back arc, the thrust belt, and the thickened Adriatic foredeep.

CO₂ seep distribution and flux concentrate in the peri-Tyrrhenian [18] and decrease towards the Apennines, where modern-day seismicity concentrates. Few seeps occur towards the foredeep. Individual seep CO₂ fluxes range from <1 to >2000 tonnes/day (t/d) [19], but 10–100 t/d is the most common [10, 12]. Overall nonvolcanic diffuse regional CO₂ release from Central and Southern Italy is globally significant [20, 21]. Studies find that seeping CO₂ may have a mixture of origins [9, 20] but the largest component derives from deep degassing from a mantle contaminated with subducted crustal carbonates [9, 22–24].

Numerous studies of seep systems in Italy have highlighted the role of buried geological structures in Mesozoic carbonates on CO₂ accumulation and leakage to the surface. These include shallow (~1 km) or deep (~5 km) anticlines [14, 19, 31] and horsts [32], but CO₂ accumulations also occur in shallow pockets within Pleistocene sands [33, 34]. CO₂ delivery to and from these structures tends to be fault associated [35–37]. Indeed, buried faults have been identified from CO₂ or Radon gas anomalies in Pleistocene cover [34, 38, 39]. At depth, CO₂ is known to affect fault properties [40–42] and seismogenesis [18, 43–47] in Italy. Seismic events are observed to affect CO₂ seep flux and style [48, 49]. While faults affect crustal fluid flow by different mechanisms [50, 51] and offer important barriers or conduits for CO₂ flow in the subsurface, along-strike permeability of faults is highly variable [51, 52], and towards the surface, many other factors influence local gas flow pathways, including topographic and hydrological factors [53] and vadose zone properties [36, 54]. As such, CO₂ fluid pathways are affected by competing crustal controls, from regional geological structures, kms deep to top soil composition.

While several regional and subregional studies of CO₂ seep occurrences are reported [55, 56], the dominant controls on CO₂ seepage have not yet been systematically studied across a range of scales and geological settings. Here, we address this gap. We adopt a novel macroscopic approach to illuminate the competing crustal controls on natural CO₂ fluid pathways by applying a novel geospatial statistical approach, the two-point spatial correlation function, to a database of CO₂ seep characteristics integrated with geological data from Central Italy. The two-point spatial correlation function is a technique developed for cosmology [57] and previously used in earth science only to investigate earthquake aftershock distributions [58]. The method quantifies the departure from homogeneity of point data, allowing the point distributions and orientations to be examined at a range of scales. As such, we do not examine each seep, cluster of seeps, or region of degassing on a case by case basis, given that these have been the subject of numerous previous

studies. Rather, we focus on using the rich geospatial dataset of CO₂ seepage in Italy to explore whether geospatial statistics can elucidate the geological controls on seep location, distribution, and characteristics over the entire region of Central Italy.

2. Methods

The database of CO₂ seeps [10] quantifies seep location, morphological type, flux, and temperature (where data are available). We do not consider wells (boreholes known to leak CO₂) or fumaroles in our analyses since man-made and volcanic seeps are not representative of leakage from geological CO₂ stores. The remaining seep data are analyzed together with geological structures and geological boundaries in mainland Italy, including 1:1 M and 1:100 k scale geological maps [59] (in this dataset, only the location of the fault trace is known; there is no information on fault characteristics, such as type, throw, and age), normal fault scarps in the Apennines [28], seismic events, and subsurface carbonate structures [60]. For more detail on these data, see SI Methods. A synthetic Poisson (random) point distribution is used as a “control” to compare against the seep data. The synthetic points are distributed within the areal extent of mainland Italy. A second Poisson distribution is created with the areal extent of the Tyrrhenian, since most seeps are located in this region (see SI Methods).

We used two approaches to test the scale dependence of point spatial relationships:

- (1) Proximity analyses determined the distance and azimuth of seeps to the nearest surface trace of a fault or lithological contact. We used the built-in ArcGIS proximity analysis tool to find the point on a fault line that is the shortest distance from a seep and then take the distance and azimuth between the seep and that point of the fault. This tells us how far the nearest fault is from each seep and where the seep is in relation to that fault
- (2) Point clustering was first examined using standard GIS tools (see SI Methods) and then analyzed more sophisticatedly using the two-point spatial correlation function. The two-point correlation method quantifies the departure from homogeneity of a distribution of points. The correlation function is expressed as the probability of finding a pair of points within an area and is usually explored over an area of incrementally increasing radius. The correlation function plots as a power law, $P \propto r^\kappa$, where P is probability, r is radius, and the constant κ describes the spatial distribution: for randomly distributed points, $\kappa = 2$, for clustered points, $\kappa < 2$, and for points randomly distributed on a line, $\kappa = 1$. The distribution of azimuths between pairs of points can also be measured by this technique. Any change in point azimuths over the increasing area of the study indicates anisotropy in the point distribution (i.e.,

whether and how the location of points in relation to each other change as the area of study increases)

3. Results

3.1. Seep Spatial Distributions. Two-point correlation function for seep and synthetic data (Figure 2(a)) shows that separation distances control distribution:

- (1) Between ~ 5 and ~ 100 km, the correlation function is the same for seep and synthetic data and $\kappa = 2$, indicating that these points are isotropically distributed. The roll-off at distances greater than 100 km is a finite size (censoring) effect [61] from the spatial extent of Italy and is less notable in the synthetic data because points are distributed across the width of Italy whereas seepage focusses west of the Apennines. Indeed, roll-off is similar for synthetic and seep when the synthetic points are distributed only in the Tyrrhenian (see SI Figure 3)
- (2) At separation distances of $< \sim 5$ km, κ decreases to ~ 0.5 –1, indicating nonrandom spatial clustering ($\kappa = 1$ indicates that seeps are aligned, and synthetic data κ remains ~ 2)

The distribution of azimuths between all pairs of seeps and synthetic points is separated above and below 10 km, the distance where the κ function begins to change (Figures 2(b) and 2(c)). At separation distances, < 10 km seeps show several orientations approximately 30 – 40° apart. Synthetic data show peaks that relate to few point pairs rather than a preferred orientation. Above 10 km, seep pairs show a preferred NW-SE (140 – 160°) orientation in which synthetic data does not exhibit. Spatial relationships are unaffected by outcrop shape/extent or seep density (see SI Results, SI Figure 3).

CO_2 seeps in mainland Italy are significantly clustered (99.9% confidence) compared to a spatially random process and form small clusters (< 5 km width) that occur ~ 20 km apart (see SI Figure 2). When analyzed by seep type, only springs are not significantly clustered (see SI Table 1).

3.2. Role of Geological Structures. Seeps spatially occur close to faults (Figure 2(d)), and all seep types are exponentially more common closer to fault traces except springs which show a much weaker, near-linear increase. Although the resolution of the fault populations limits the confidence of spatial interrogation at distances < 1 km, 90% of vent, diffuse, and bubbling water seeps are located < 1 km, increasing to 2 km for springs. These relationships are consistent for both geological datasets (1 M, 100 k). Seep-fault azimuths are principally SW (-NE).

Seeps are also preferentially located towards lithological boundaries; 76% of all seeps and all CO_2 springs are located < 1 km from lithological boundaries for both geological datasets (Figures 2(d) and 3(a)). Seeps show no favored orientation from lithological contacts, unlike faults. Seep flux and temperature datasets are incomplete but neither correlate with proximity to faults or lithological contacts.

Known seeps occur above structural highs of Mesozoic carbonate subsurface topography. For example, two CO_2 seeps occur above an anticline crest known to host CO_2 [19, 62] and others appear near to the crest, or local highs on the flanks, of carbonate structures and décollements (Figure 3(b)).

In the seismically active Apennines, seeps are rarely located along fault scarps. The few (37) CO_2 seeps which are located < 10 km of a fault scarp are mostly (70%) springs with high fluxes (all but one seep with quantified flux emit > 10 t/d). Unlike seeps towards the Tyrrhenian, Apennine seeps are located SSE of the faults and typically positioned towards the fault tip or in ramp structures in fault stepover zones (Figure 3(c)).

- (a) *Major and minor fault traces.* Near Suio in Castelforte (Lazio), where 4 bubbling water and 2 vent seeps are located along, or close to, fault traces and lithological boundaries in 1:1 M and 1:100 k geological datasets [59] which do not specify the fault types
- (b) *Leakage from subsurface structures.* Close to Rocca San Felice in Avellino (Campania), where 2 CO_2 vents are located above the Monte Forcuso anticline that is known to host the CO_2 reservoir
- (c) *Fluid flow at fault tip points.* East side of Rieti Basin (Lazio) where 3 springs (2 high, 1 very high flux) emerge towards the fault tip points of a normal fault scarp, rather than along the fault trace. The scarp was mapped in detail by [28] (shown in the image)

4. Discussion

4.1. Subsurface Plumbing of CO_2 Fluids. Seeps are preferentially located near to the faults and show several preferred point pair azimuths within clusters (Figure 2). Regional NW-SE structures may be a primary control on CO_2 seepage, but towards the surface, it seems that any fault (i.e., any range of orientation) is the secondary control that governs where seeps emerge within a cluster. Fault orientations are more varied in the 1:100 k dataset than the 1:1 M (see SI results). So, as well as subsidiary faults and fractures, which can exhibit a wide range of orientations to the primary deformation structure, there are also structures which predate the Miocene compression and extension [63]. CO_2 migrating from buried anticline or horst structures may do so via whichever of these features provide transmissive pathways.

As observed by previous authors, our analyses find that geological structures determine the presence and location of CO_2 seeps in Italy. We also observe that distance from a fault influences the seep type (Figure 2(d)). Seep type may therefore indicate the degree of near-surface spread from geological structures and therefore the relative control of other geological and hydrological factors other than the fault trace [53]. For example, compared with other seep types, the location of CO_2 springs shows the weakest relationship with faults and the strongest relationship with lithological boundaries.

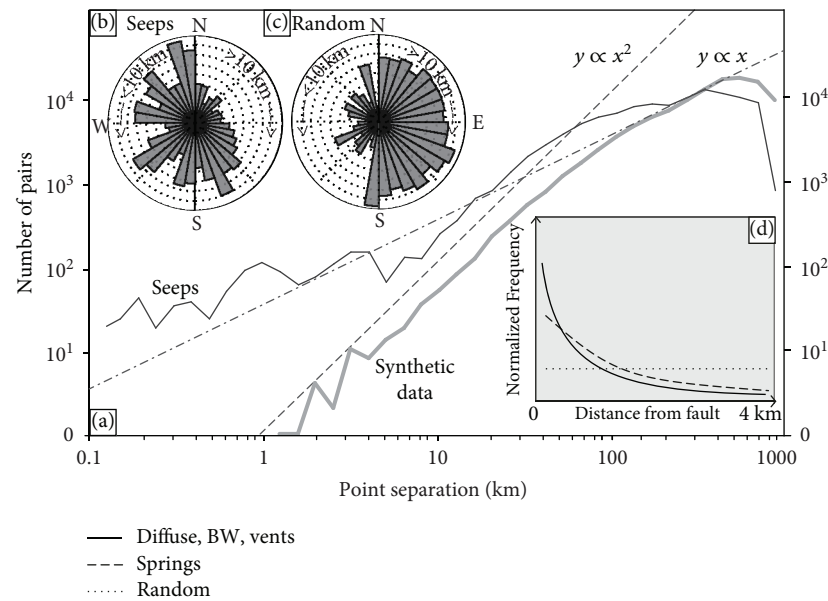


FIGURE 2: (a) Point-distance correlation functions for seep and synthetic (random) data in mainland Italy, showing the break in the slope for seep data around ~5 km and roll-off towards ~100 km in both datasets. The synthetic dataset is not clustered so few pairs are <10 km apart. Inset shows distribution of azimuths for points <10 km (anticlockwise) and >10 km (clockwise) for (b) seeps and (c) synthetic data. Seeps show several favored orientations <10 km and NW-SE trend >10 km separation. (d) Normalized line histogram of seep types and distances from lithological boundaries and faults. BW refers to bubbling water seeps.

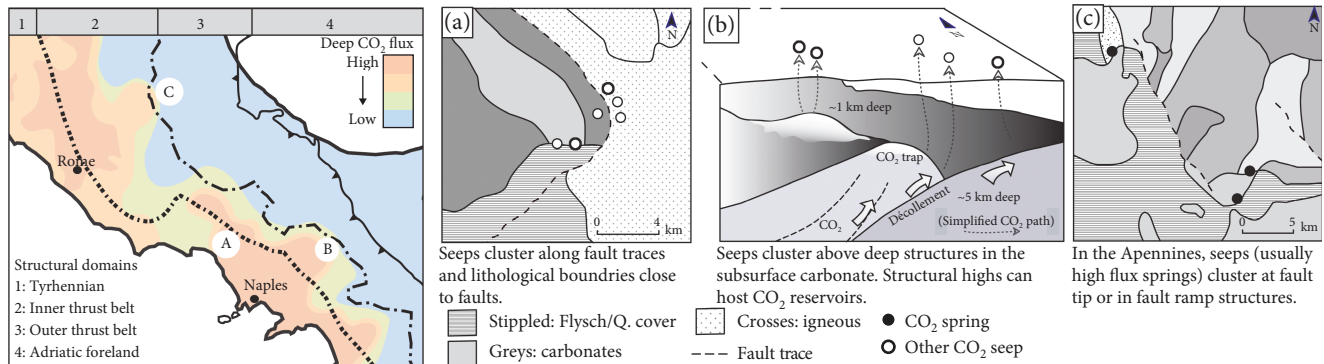


FIGURE 3: Map of Central Italy showing CO₂ seepage in the major structural domains [17], distribution of deep CO₂ flux [18], and the location of three examples illustrating the range of structural controls on CO₂ seeps within the three domains of degassing. The specific lithologies in (a) and (c) are not indicated here but can be found from [59]. The three scenarios are not mutually exclusive.

It is not surprising that crustal migration pathways of aqueous CO₂ fluids differ from gaseous or free-phase CO₂. The location of CO₂ springs is controlled by the hydrogeological characteristics of the aquifers. Assuming that the aquifer is well mixed, external CO₂ could have entered the aquifer at any point(s) within the aquifer subsurface extent, in which case CO₂-rich springs do not indicate the location of CO₂ fluid flow pathways from depth, i.e., the spring may be located far from the fault trace(s) supplying the CO₂.

The robustness of our results is of course limited by the resolution of the geological data and the completeness of the gas seep information. However, our meta-analysis identifies three different seep settings in Central Italy (Figure 3). These settings are distinct but are not mutually exclusive

and align with the current understanding of crustal controls on fluid flow.

- (1) *Major and minor fault traces.* In the Tyrrhenian, the extended back arc region, 90% of vent, bubbling water, and diffuse seeps are located within 1 km of a fault (Figure 3(a)). The location of seeps suggests that in this geological setting, CO₂ fluids are channeled by barrier/conduit properties of the fault wall and so seeps emerge along it, close to fault traces
- (2) *Leakage from subsurface structures.* In many cases, deep geological structures supply CO₂ to surface seeps. As such, due to the structural trend of compression and extension structures in Central Italy,

the resulting seep clusters supplied by buried CO₂ accumulations will be located NW-SE of each other (Figure 3(b)). The orientation of faults related to, or pre- or postdating, these subsurface structures is likely to be responsible for the leakage of CO₂ to the surface. For example, at Mefite d'Ansanto, the example in Figure 3(b), observed polarization of ambient seismic noise, may indicate the presence of faults governing gas escape from the Monte Forcuso CO₂ reservoir [64]

- (3) *Fluid flow at fault tip points.* There are fewer CO₂ seeps located within the Apennines compared to the Tyrrhenian sector, and Apennine seeps tend to be springs with high fluxes and occur at lithological boundaries (Figure 3(c)). This indicates that there are limited pathways to surface for free-phase CO₂ fluids in this region, which is also the most seismically active part of Central Italy. Instead, CO₂ from depth enters the aquifers and its emergence as CO₂ springs is then controlled by hydrogeology. We find that springs tend to emerge close to fault tips or in ramp structures in stepover zones. While these fault scarps are clearly an important control on crustal fluid flow in the Apennines, it is not necessarily the case that fault tips or ramp structures in stepover zones offer pathways for CO₂ migrating all the way from depth to the surface

We propose that orientation of regional geological structures leads to the observed surface distribution of seep clusters in Central Italy (Figure 2). Extensional faults of the Apennines and major normal faults in the Tyrrhenian sector align NW-SE (see SI Results), and although compressional structures are more variable in their orientation, these are also predominantly NW-SE in Central Italy, where CO₂ degassing concentrates. This means that our analyses cannot distinguish which fault types exert greatest control on CO₂ seep distributions and characteristics. Ghisetti et al. [37] found that extension-related structures in Italy permit fluid flow during deformation, whereas contraction-related structures were initially closed but opened during subsequent exhumation and extension. Regional extensional and compressional features in Italy may therefore be important for governing crustal fluid flow, supplying deep-derived CO₂ to buried structures within the tectonized Mesozoic carbonates and ultimately to seep clusters (Figure 3(b)). However, at a global scale, Tamburello et al. (2018) have shown that there is a spatial correlation between CO₂ discharges and the presence of active fault systems and particularly with normal slip faulting.

4.2. Implications for Carbon Capture and Storage. Understanding the geological controls on CO₂ fluid flow can aid the prevention of leakage from engineered CO₂ stores by informing effective site selection criteria. Moreover, should unintended leakage to the surface occur, understanding the

geological controls on CO₂ fluid flow can inform the assessment of the potential CO₂ seep locations and characteristics.

In Italy, we observe that CO₂ seepage is clustered and that the location, distribution, and type of seepage within and between these clusters are controlled by a number of factors. These include, in the order of importance (as highlighted by our study), the orientation of regional structures, the geological setting, the density, and orientation of local geological structures and whether CO₂ is migrating in spring water or as a separate phase. It is therefore important not only to characterize the storage formation and overburden but to consider the storage system in the context of the geological setting and near-surface geology.

Our work contributes towards predictive models of CO₂ leak pathways. These models are important to de-risk sites selected for engineered storage, since site selection protocols can minimize the risk of leakage [6]. Further, whether CO₂ migrates and/or is emitted to the surface as gas or as a dissolved constituent of springs has implications for the environmental and social risk and impact of CO₂ leakage [12, 65, 66] and so the design of robust and cost-effective monitoring programs to detect CO₂ migrating to the surface should CO₂ migrate from its primary storage formation [67].

Data Availability

The analyses presented in the paper used publicly available datasets, as specified in the article text and the SI Methods.

Conflicts of Interest

There are no conflicts of interest to declare.

Authors' Contributions

J. J. Roberts designed the research, conducted the data analysis and wrote the paper. A. F. Bell contributed to the research design and data analysis, and R. A. Wood and R. S. Haszeldine contributed towards the research design and writing of this paper.

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Supplementary Materials

SI Figure 1: polar plot of normalized azimuths from the analyzed fault datasets. SI Table 1: results of point cluster analysis. SI Figure 2: Ripley's *K* function for seeps and the synthetic random dataset. SI Figure 3: two-point correlation results for seep data compared with results of synthetic points located in the Tyrrhenian sector (where seeps are most

numerous) and seeps hosted in turbiditic rock units (the most common outcropping rock type in Central Italy). (Supplementary Materials)

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